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Anomalous groundwater-rocks interactions for conditions of the Cenomanian-Callovian aquifer exploited by the Obolon water intake wells in Kyiv

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SUMMARY

The purpose of this work is to estimate interactions in the water-rock system using an integrated approach, which includes the balance method and the method of geochemical (thermodynamic) modelling, and to illuminate the role of these interactions in the formation of water composition of the Cenomanian-Callovian aquifer. The results show the differences both in water composition and mechanisms of its formation within the small area of the Obolon water intake wells location. Two groups were conventionally distinguished. In water of the Icen group the Cl- specific content is almost two times higher than in water of the IIcen group. In water, classified as group Icen, the role of ion exchange processes is insignificant. The specific feature of water classified as group IIcen is the imbalance exists between sodium and chlorine concentrations. With increase of Cl- concentration sodium concentration remains unchanged and varies around the average value. Formation of the chemical composition of water of the group IIcen can be described as follows: first, groundwater balanced by sodium and chlorine enters the aquifer, then, as a result of ionic exchange and precipitation of montmorillonite and illite, sodium is removed from the water, while the concentration of chlorine doesn't change.

Introduction

Groundwater chemical composition is influenced by many factors, including the atmospheric precipitation content, climatic conditions, regional hydrogeological and geological features, vegetation (or organic matter decay), and anthropogenic factors (Belkhiri et al., 2010; Ntanganedzeni et al., 2018). Most notably are the processes of interaction in the water-rock system. As a rule, the concentration of major elements in groundwater is caused by cation exchange, minerals dissolution/precipitation, redox reactions, and evaporation. Statistical and balance methods, various types of diagrams, and geochemical (thermodynamic) modelling are used to perform various hydrogeological and hydrochemical assessments. In recent years, various aspects of groundwater quality and composition have been studied in Kyiv. The data on the concentration of microelements (Kuraeva et al., 2008; Zlobina and Tugai, 2014), anthropogenic factors influence on the groundwater regime (Koshliakova, 2011), dynamics of changes in the chemical composition of water in the Cenomanian-Callovian aquifer (for example Koshliakov et al., 2014) were obtained and analyzed. Although studies of the composition and protectability of groundwater and surface water in the Kyiv area were carried out quite intensively, they did not take into account the interaction in the water-rock system of the aquifer. The purpose of this work is to estimate preliminary these interactions using an integrated approach, which includes the balance method and the method of geochemical (thermodynamic) modelling, and to illuminate the role of these interactions in the formation of water composition of the Cenomanian-Callovian aquifer.

Method and input data

The object of research was the water of Cenomanian-Callovian aquifer exploited by pumping wells of the “Obolon” water intake structure in Kyiv. “Obolon” water intake structure is located in the right-bank part of the city and includes two water pumping and supplying stations: Obolon-1 and Obolon-2. Geology and hydrogeology of the research area are studied and described in detail (for example, Kovalev et al., 2001; Fedorenko et al., 2019). The Cenomanian-Callovian aquifer is deep well-protected artesian aquifer used as one of the main underground sources of water supply to Kyiv city.

An integrated approach was applied for this study. It includes the balance method (Hounslow, 1995) and thermodynamic modelling based on computer program PHREEQC (Parkhurst and Appelo, 1999).

To assess the interactions in the water-rock system of the aquifer, the reported data on the composition of water in the Cenomanian-Callovian aquifer sampled from wells of the “Obolon” water intake structure were used (Shestopalov et al., 1997; Rudenko et al., 2007; Fedorenko et al., 2019). In total, 30 datasets (for 30 wells) for 1996-2018 were considered. Data on 3 wells were excluded from further consideration because of charge imbalance. Data reported in different years for the same well were averaged due to the lack of temporal trends. As a result, 19 datasets were used to perform the study.

Results and discussion

Piper and Durov diagrams and Kurlov’s formula were used to determine water types. Groundwater of the Cenomanian-Callovian aquifer refers to hydrocarbonate type in terms of anion content. Content of chlorides and sulphates in water of this aquifer is much lower. According to the cations content, water belongs to the calcium type. Two groups were conventionally distinguished (Table 1): in water of the Icen group the Cl- specific content is almost two times higher than in water of the IIcen group.

Table 1. Coefficients of Kurlov's formula for water of the Cenomanian-Callovian aquafer on the Obolon water intake (average for groups)

Reference designation	Cl^-	SO_4^{2-}	$HCO_3^-+CO_3^{2-}$	Na^+	K^+	Ca^{2+}	Mg^{2+}
Icen, N=10	10.58	7.09	82.33	9.65	3.04	64.03	23.41
IIcen, N=9	21.50	5.14	73.02	8.18	2.62	66.00	23.21

N – number of samples

Figure 1a shows that the samples of water belonging to the Icen group (higher specific content of Cl^-) are located very close to the baseline $Na^+=Cl^-$, which indicates the absence of a significant contribution of ion exchange and precipitation/dissolution of secondary minerals in the formation of the Na^+ concentration. Samples of water belonging to the group IIcen lay below the baseline, which indicates the removal of sodium from solutions. The chlorine content in these samples increases, while the sodium content remains unchanged and varies around the average value within the error of 5%.

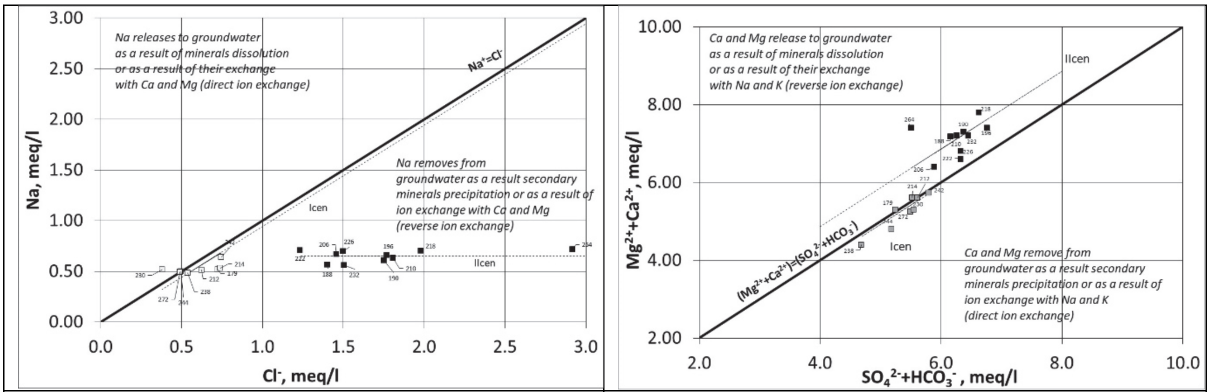

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Figure 1 *Relationship between the main components of groundwater: a) Na^+ vs Cl^-; b) $Ca^{2+}+Mg^{2+}$ vs $CO_3^-+SO_4^{2-}$*

Samples of water belonging to the Icen group (higher Cl^- specific content) locate very close to the baseline $Ca^{2+}+Mg^{2+}=HCO_3^-+SO_4^{2-}$, indicating that there is no significant contribution of ion exchange or secondary minerals precipitation/dissolution in the formation of the Ca^{2+} concentration. A comparison of the graphs in Figure. 1a and 1b shows that there is no significant removal of calcium and no significant removal of sodium for the samples of group Icen. So we can conclude that ion exchange processes are unessential for the formation of Ca^{2+} and Na^+ concentrations in this water of group Icen. In samples belonging to group IIcen, there is an excess of calcium and magnesium compared to the concentration of HCO_3^- and SO_4^{2-}, which indicates additional sources of magnesium and calcium than the dissolution of their sulphate and carbonate minerals.

Modelling of equilibrium in natural water of the Cenomanian-Callovian aquifer

Modelling results showed that water is saturated with respect to carbonate minerals (dolomite> calcite> aragonite, Figure 2a), relative to iron minerals (Fe (OH)3am> goethite> hematite), gibsite, quartz, K-mica, kaolinite, Ca-montmorillonite and illite (K-mica> kaolinite> Ca-montmorillonite> illite, Figure 2b). Saturation indices with respect to all minerals for Icen water are lower than for IIcen water.

It should be noted that the PHREEQC modeling results could not give a direct answer to the question of what kind of secondary minerals is responsible for sodium removal from the water of group IIcen. As shown above for group IIcen, the concentration of Na+ and K+ is partly determined by reverse cation exchange, when calcium and magnesium are displaced from rocks into groundwater as a result of exchange with Na^+ and K^+. However, the key assumption remains that sodium removes from water mainly as a result of secondary minerals formation. According to the simulation results, the samples of this group are saturated with respect to K-mica, Ca-montmorillonite, potassium feldspar, and illite. Saturation indices for the IIcen group are slightly higher than for the Icen group, but the difference is insignificant. However, in the database used in PHREEQC, Ca-montmorillonite and illite are described as minerals of constant composition (respectively, $Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$, $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$). Actually, in nature, they occur as minerals of variable composition (respectively, $(Na,Ca)_{0,3}(Al,Mg)_2[Si_4O_{10}](OH)_2$•$nH_2O$ and $(Na,K)_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$), so the results obtained may indicate the possibility of sodium removal during the precipitation of montmorillonite and illite.

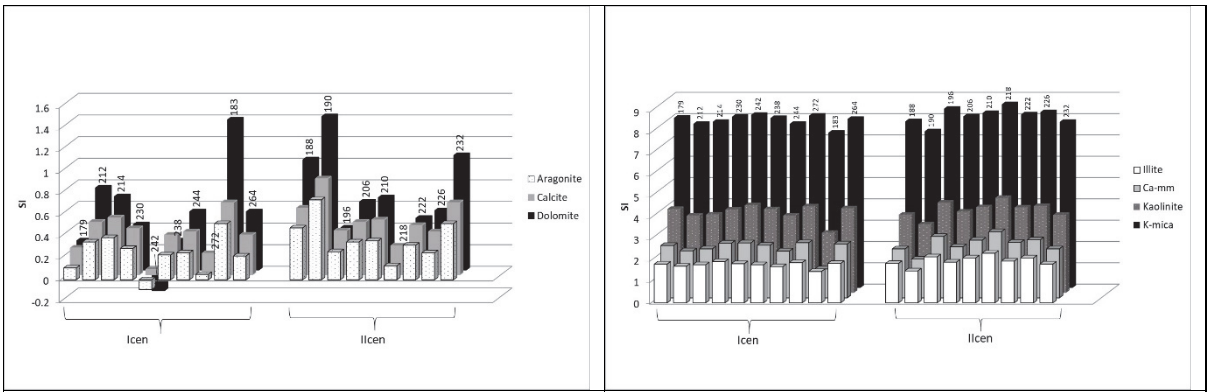

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__Figure 2__ Saturation indices: a) carbonate minerals; b) silicate minerals

Analysis of spatial distribution of different types of water in the Cenomanian-Callovian aquifer over the area of the Obolon water intake (Figure 3) showed that wells with water of group Icen (Cl- specific content is two times higher than in water of IIcen group) are concentrated in the lower and upper part of the scheme of wells location, and wells with water of group Icen occupy an intermediate position.

wells with water of group Icen

wells with water of group IIcen

__Figure 3__ Scheme of wells location and indicated different groups of water

No obvious correlation is observed between the type of water and the volume of groundwater withdrawal which contradicts the conclusions of works (Koshliakov et al., 2014). This inconsistency can be explained by the fact that the authors analyzed data for the XIX-XX centuries, when groundwater withdrawal in the city grew up steadily. Since 2000 the volume of groundwater withdrawal has decreased significantly and the processes that determined the groundwater composition in the XIX-XX centuries may now be running in the opposite direction, trying to return the system, if not to the original, then to a new equilibrium state.

Conclusions

The above results show the differences both in water composition and mechanisms of its formation within the small area of the Obolon water intake wells location . In water of the Cenomanian-Callovian aquafer, classified as group Icen, the role of ion exchange processes is insignificant and the balance between sodium and chlorine concentrations is preserved. The specific feature of water classified as group IIcen is twice as high chlorine concentrations as in water of group Icen. Also, the imbalance exists between sodium and chlorine concentrations. With increase of Cl- concentration sodium concentration remains unchanged and varies around the average value.

Formation of the chemical composition of water of the group IIcen can be described as follows: first, groundwater balanced by sodium and chlorine enters the aquifer, then, as a result of ionic exchange and precipitation of montmorillonite and illite, sodium is removed from the water, while the concentration of chlorine doesn't change. Slight variations in sodium concentrations can be explained by the buffering properties of montmorillonite minerals, which, according to the modelling results, can precipitate in aquifer conditions. The cause of this anomaly may be occurrence of a fault through which deep sodium chloride water would ascend into the Cenomanian- Callovian aquifer, and then, according to the mechanisms described above, sodium would be removed from them.

It should be noted that this conclusion is only a hypothesis, which is planned to be examined in the future by modelling based on computer program GEMS with explicit consideration of the rock composition and the representation of clay minerals and micas as solid solutions and a thorough analysis of fault zones over the Kyiv area.

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